A density functional theory study of the dissociation of H_2 on gold clusters: Importance of fluxionality and ensemble effects

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Density functional theory was employed to calculate the adsorption/dissociation of H_2 on gold surfaces, Au(111) and Au(100), and on gold particles from 0.7 (Au_{14}) to 1.2 nm (Au_{29}). Flat surfaces of the bulk metal were not active towards H_2, but a different effect was observed in gold nanoclusters, where the hydrogen was adsorbed through a dissociative pathway. Several parameters such as the coordination of the Au atoms, ensemble effects and fluxionality of the particle were analyzed to explain the observed activity. The effect of the employed functional was also studied. The flexibility of the structure, i.e., its adaptability towards the adsorbate, plays a key role in the bonding and dissociation of H_2. The interaction with hydrogen leads to drastic changes in the structure of the Au nanoparticles. Furthermore, it appears that not only low coordinated Au atoms are needed because H_2 adsorption/dissociation was only observed when a cooperation between several (4) active Au atoms was allowed. © *2006 American Institute of Physics*.
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INTRODUCTION

Whereas bulk gold is considered an inert material, gold nanoparticles exhibit a high activity in a wide variety of reactions. Depending on particle size, gold is able to catalyze different reactions. For instance, CO oxidation or hydrogenation reactions require particles below 2 nm in size, whereas propylene epoxidation takes place on bigger particles (up to 4–5 nm).[1] Shape,[1] size,[2] and support interactions[3] have been suggested as the main factors explaining the astounding properties of nanosized gold particles.

Several theoretical works have addressed the issue of the intrinsic reactivity of free Au clusters.[4–6] It is very important to establish the characteristic behavior of Au nanoparticles in the presence of adsorbates. Generally small clusters, up to 55 gold atoms, have been considered for the study of the adsorption of molecules. Some key parameters taken into consideration in the literature have been the coordination number of the Au atoms (i.e., the less coordinated are the more active),[3,4] fluxionality of the cluster or nanoparticle,[4,5] and charge transfer effects between adsorbate and metal.[5] Thus, it has been established that unsupported nanoparticles of gold can carry out the oxidation of CO,[4] which can be favored by the effects of metal-support interactions.[3,5,7]

Most of the theoretical studies are concerned with the interaction of oxygen with gold and few deal with hydrogen.[8–10] Also from an experimental point of view, much fewer data on H_2 adsorption compared to O_2 adsorption are available. Nevertheless, H_2 is a reactant or product in many reactions catalyzed by Au nanoparticles.[1,11,12] The adsorption of molecular hydrogen on bulk gold does not occur,[13] but chemisorption on nanoparticles has been reported, although quantitative experimental data are still lacking.[12] Theoretical work on hydrogen adsorption on gold nanoparticles is limited as it deals either with small clusters (up to three gold atoms) (Ref. 8) or fixed geometry of the cluster (13 gold atoms).[9] Modeling the right size and right shape of gold clusters is therefore fundamental in obtaining reasonable results. It is not clear if the ability of a gold cluster to adapt its structure (fluxionality) is a key phenomenon in the thermodynamics for the adsorption/dissociation of H_2.

THEORETICAL METHODS

In the present study, density functional theory (DFT) was employed to study and compare molecular hydrogen adsorption on gold nanoparticles (sizes from 0.7 to 1.2 nm) and on periodic surfaces of bulk gold. The geometry of the clusters was fully relaxed to allow structural changes during the adsorption. All the calculations were performed with the DMOL^3 program,[14,15] using the generalized gradient approximation with the PW91 functional[16] allowing spin polarization, as used in previous works.[3,17] The most relevant results were recalculated with the BP (Becke-88 for exchange and Perdew-91 for correlation) and RPBE functionals,[18,19] in order to study the influence of the functional on the mechanism of H_2 adsorption. A numerical basis set, which describes the

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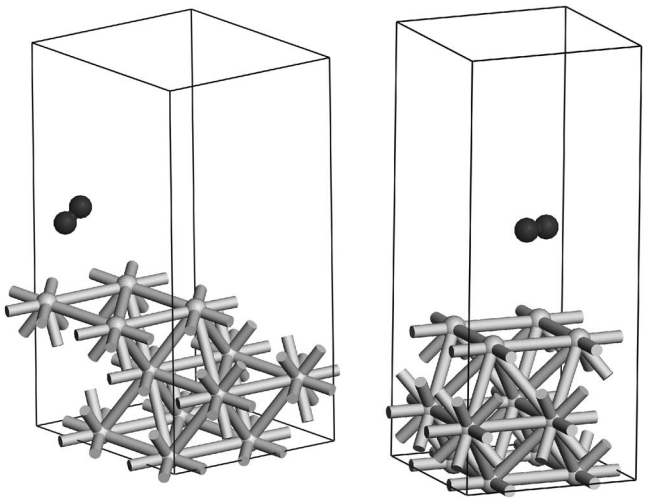

FIG. 1. H_2 on (a) Au(111) and (b) Au(100) surfaces.

orbitals in the valence shell with double numerical functions and includes a polarization *d* function for the light atoms, was employed here. It is comparable in accuracy to a Gaussian 6-31G* basis set and it was previously very useful for examining the geometry of Au clusters and their bonding to SO_2.[20] Gold atoms were expressed by effective core potentials to account for relativistic effects.[21] A similar methodology has been widely employed to accurately describe molecular adsorption on gold clusters.[3,8,22] In the calculations, we allowed the full relaxation of the gold nanoparticles and the adsorbed H_2. In most cases, the geometry optimization of these systems was done without symmetry constraints.

RESULTS AND DISCUSSION

First, we will start by examining the adsorption of H_2 on Au(111) and Au(100), the most stable surfaces of the bulk metal. In these surfaces, each Au atom has at least eight neighbors. To model the surface of gold a representative unit cell of three layers and four atoms per layer, which is shown in Fig. 1, was employed. In order to account for the rigidity of the metal structure only the first atomic layer was allowed to relax during the geometry optimization.[13,17] Several adsorption sites (*a*-top, bridge, and hollow positions) were tested on both surfaces with H_2 bonded with its molecular axis parallel or perpendicular, yielding essentially the same result. The interaction between H_2 and bulk gold is too weak for the molecule to be chemisorbed, see Table I. In the two most stable configurations found for physisorbed H_2 (Fig. 1) the molecule is away from the surface with a H–H bond distance (Table I) essentially equal to that seen for free H_2 (0.75 Å). Physisorbed states are difficult to handle with conventional DFT since there are no dispersion effects.[23] The important point here is that the Au(100) surface is more open than the Au(111), but it is still not able to chemisorb or dissociate H_2. These results are in good agreement with experimental evidence and a previous theoretical work for H_2/Au(111),[13] which indicates that the hydrogen molecule does not chemisorb on bulk gold, no matter the configuration of the adsorption sites.

TABLE I. Adsorption energies of H_2 on gold surfaces and nanoparticles. (The corresponding bonding geometries are shown in Figs. 1–4.)

Structure	$H-H_{\text{bond distance}}$ (Å)	$\Delta E_{\text{adsorption}}$ (kJ/mol)
Au (111) surface PW91	0.751	−2.01
Au (100) surface PW91	0.750	−1.21
Au_{14} PW91	3.532	−31.80
Distorted Au_{29} PW91	3.441	−43.22[a]
Fixed Au_{29} PW91	3.245	25.15[b]
Distorted Au_{29} BP	3.645	−33.22[a]
Distorted Au_{29} RPBE	3.718	−19.58[a]

[a]The distorted structure of Au_{29} was taken as reference for the estimation of the dissociative adsorption energies.
[b]The C_{4v} pyramidal structure of Au_{29} was taken as reference for the estimation of the dissociative adsorption energy.

Two options have been followed for modeling the nanosized gold clusters. First a most simple unit of 14 gold atoms in a fcc structure has been considered [see Fig. 2(a)]. This Au_{14} cluster contains atoms with a high coordination number

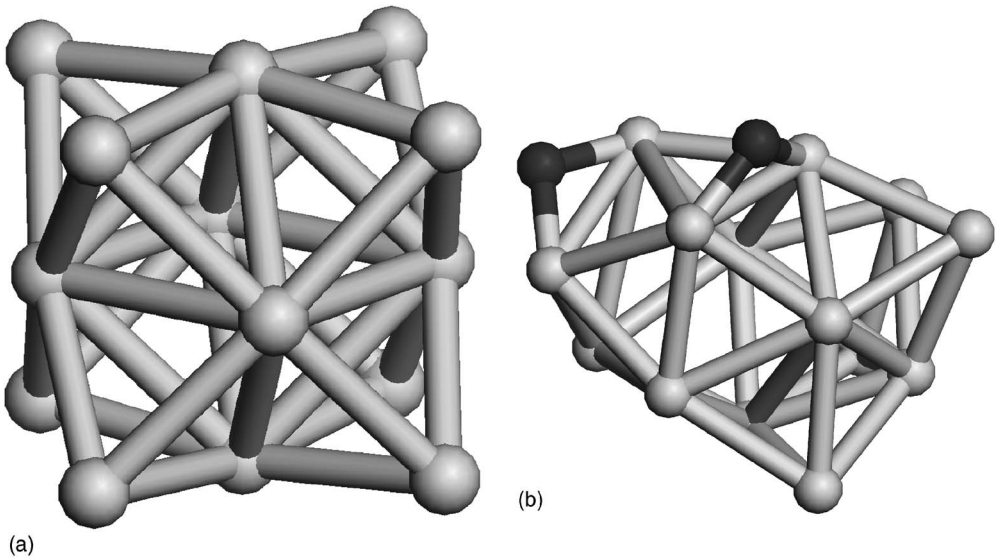

FIG. 2. Au_{14} cluster (a) before and (b) after H_2 adsorption.

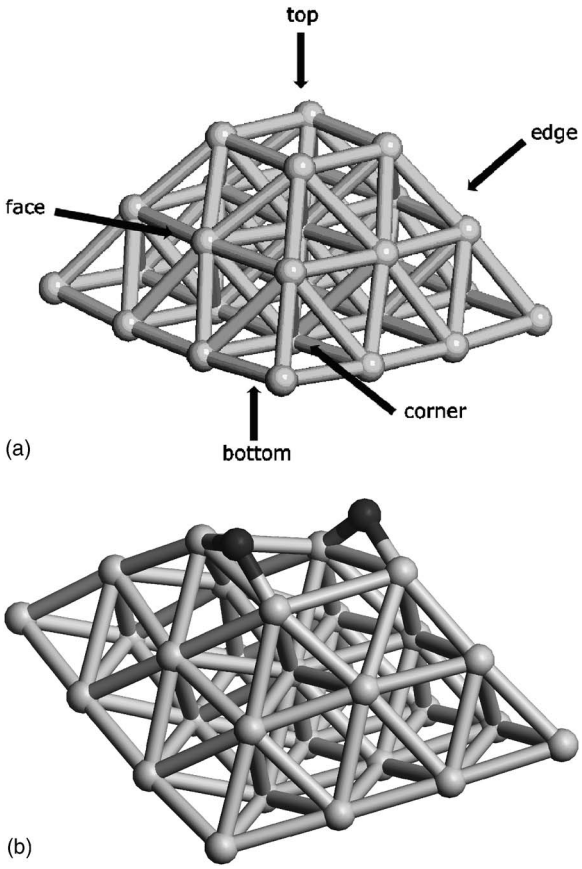

FIG. 3. Au_{29} cluster (a) before and (b) after H_2 adsorption.

(8) as seen in extended surfaces and atoms with a low coordination number (3). Also a bigger structure of 29 gold atoms was investigated [Fig. 3(a)]. This model aims to mimic the shape of Au nanoparticles supported on TiO_2 (Refs. 3 and 24) or CeO_2.[25] It has a pyramidal structure, and it is formed by the interconnection of (111) and (100) faces of gold. This structure is consistent with a Wulff-Kaichew construction[3] on the surface of TiO_2 and, more importantly, it is also in agreement with nanoparticles observed in images of high-resolution transmission electron microscopy for Au/TiO_2 catalysts.[3,19] Similar gold clusters have been observed on $CeO_2(111)$ with scanning tunneling microscopy[25] and are active for the production of hydrogen through the water-gas shift reaction.[11] The TiO_2 and CeO_2 supports are taken into consideration here only by being the determinant factor for giving shape to the Au_{29} cluster. As we will see below, the most reactive part of this cluster is the top, which will never be in contact with an oxide support.[19,20]

Molecular hydrogen chemisorbs following a dissociative pathway on the Au_{14} cluster. The $H_{2,gas} \rightarrow 2H_{ads}$ reaction readily takes place on a flexible array of four Au atoms [Fig. 2(b)]. The dissociation of the molecule was found to be a spontaneous process (no significant energy barrier was found during the geometry optimization). Once the H_2 has approached the gold cluster, the H–H bond is spontaneously elongated up to breaking. During this dissociation process the cluster deforms in order to optimize the geometry for holding the H atoms. This result is in contrast to some studies previously reported for H_2/Au_3 and H_2/Au_{13},[8,9] where the molecule interacted with a limited number of Au atoms or the relaxation of the Au cluster was not allowed. The energy change for the $H_{2,gas} \rightarrow 2H_{ads}$ reaction on Au_{14} is ~ -32 kJ/mol (Table I). As mentioned above, it is worth noting the high distortion suffered by the cluster when adsorbing H_2 [Fig. 2(b)]. The high fluxionality of the small particle makes the stabilization of the dissociated hydrogen feasible. This is not possible on the Au(100) and Au(111) surfaces or on the rigid icosahedral Au_{13} cluster used in Ref. 9. On the rigid Au_{13} cluster there is a release of ~ 33 kJ/mol for the dissociation of H_2, but an activation barrier of 29 kJ/mol makes the dissociation of the molecule difficult. This large activation barrier is probably caused by the fact that the adsorbate only interacts with two Au atoms in a rigid particle.[9] The calculated energy barriers for H_2 dissociation on a Au_3 cluster is at least 42 kJ/mol, depending on the functional used.[8]

As a second representation of a gold cluster, the reactivity of a structure of 29 gold atoms was examined. Several bonding sites have been tried for molecular hydrogen adsorption on this cluster [Fig. 3(a)]. First, the H_2 adsorption was tried on the bottom face, which resembles the (100) surface of gold. On the atoms of this face, no hydrogen adsorption was observed. Then, the molecule was moved to the lateral (111) face of the pyramid. Again, no significant interaction between H_2 and gold atoms was obtained. Edge atoms are frequently considered the most active due to their low coordination number.[4,6] Thus, the next step was to study H_2 adsorption at the edge atoms of the Au_{29} cluster. The edge and corner positions were checked but in no case was the adsorption of the hydrogen molecule seen.

Finally, the top of the cluster was tried as the site for H_2 approach. Only in this case, a relatively strong interaction was obtained. The direct adsorption of molecular hydrogen on the top of this cluster leads to a distorted structure of the gold aggregate and a spontaneous dissociation of H_2. This is an exothermic process with a stabilization energy of ~ 43 kJ/mol (Table I). For the H_2/Au_{29} system, we also did calculations using the BP and RPBE functionals. The energies released by the dissociation process are listed in Table I. As expected the RPBE functional predicts a much weaker interaction than the PW91.[19] Typically, adsorption energies calculated with the RPBE functional are 20–35 kJ/mol smaller than with the PW91 functional.[19] Independent of the used functional (PW91, BP, or RPBE), we found no activation barrier for the dissociation of H_2 on the Au_{29}. During geometry optimization, the H–H bond broke spontaneously.

Once the H_2 dissociated, the gold cluster was substantially distorted [Fig. 3(b)]. The presence of hydrogen produced a rearrangement of the electron density, which led to a change in the structure of the cluster. From a C_{4v} symmetric pyramid the cluster elongated to form a distorted boat-shaped structure with C_{2h} symmetry. This distortion produces an arrangement of the gold atoms in the particle that gives a high number of gold atoms exposed in the (111) face. This face is the most stable surface of gold, and hence the fluxionality contributes to the cluster stablilization. As it was observed for the Au_{14} cluster, the flexibility of the structure, its adaptability towards the adsorbate plays a key role in the

TABLE II. Structural and energetic parameters of C_{4v} and distorted Au_{29} clusters.

Structure	$Au-Au_{bond\ distance}$ (Å)			ΔE (kJ/mol)
	Top	Bottom	Face	
C_{4v} Au_{29}	2.826	2.758	2.918	···
Distorted Au_{29}	2.778	2.806	2.855	−97.19

bonding and dissociation of H_2. This observation can explain the activity of small particles which may be due, among other reasons, to the fact that the nanosized clusters are more adaptable towards H_2 adsorption than flat (111) and (100) surfaces of bulk gold.

The properties of the distorted cluster are shown on Table II. As can be observed the stabilization of the structure after the distortion is as high as 97 kJ/mol. Also, the bond distances of gold atoms in every position are affected by the distortion, leading to maximum differences of 0.1 Å between both structures. The distorted structure was used as the reference to calculate the bonding energies in Table I.

In order to evaluate the influence of the fluxionality of the cluster during the chemisorption process we performed a new calculation in which the structure of the gold atoms was constrained. The top layer of four atoms was able to move freely, while the two other layers were fixed. Only the top position was tried as the approach site because it was proved above to be the active one. This restriction keeps the system under a C_{2v} symmetry point group during the geometry optimization, although the relaxed cluster yielded to a C_2 symmetry. Two individual H atoms were bonded to the cluster as shown in Fig. 4. The partial relaxation of the geometry affects the thermodynamics and the $H_2 \rightarrow 2H_a$ reaction has an endothermicity of 25 kJ/mol (see Table I). When the geometry was fully relaxed the dissociation released 43 kJ/mol of heat. It is worth noting the difference in energy of 68 kJ/mol between the fixed and relaxed pathways. Hence, the electronic properties of the gold atoms in the nanoparticle help the dissociation of H_2, but it is the fluxionality of the cluster which makes the process energetically favorable.

However, there is still a question to be answered, why is the top of the cluster the preferential bonding site? The fact that there is only one active place for the adsorbate to encounter the cluster needs a careful lookup. It seems that not only low coordinated Au atoms are needed. Neither the inherent strain of the nanoparticle is enough to make the gold atoms active. The adsorption/dissociation of H_2 is only obtained when cooperation between several active Au atoms is allowed. The main difference of the corner and *a*-top bonding positions is that on the former only two or three atoms of gold are close enough to meet the hydrogen molecule. On the top of the cluster, four active gold atoms contribute to the dissociation of hydrogen. It is an ensemble effect of the first layer of atoms and also of the whole cluster, adapting its shape to hold the hydrogen. This cooperative effect has been observed in previous theoretical studies for the adsorption of other molecules (CO and O_2).[4]

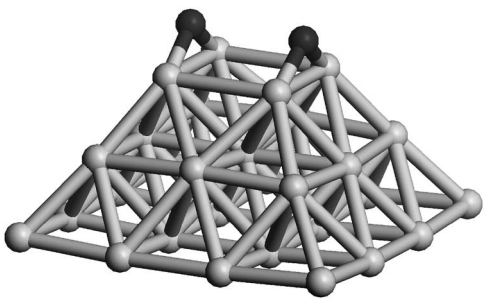

FIG. 4. Fixed Au_{29} cluster after H_2 adsorption.

The reaction mechanism seen in the theoretical calculations opens the possibility of finding dissociated H atoms on gold nanoparticles when these are under moderate or high pressures of H_2. The small values of the ΔE for the dissociation of H_2 (−32 to −43 kJ/mol, PW91) make the reverse reaction easy at elevated temperatures. The lack of a strong Au–H bond facilitates the formation of H_2 during the water-gas shift reaction on Au/CeO_2 catalysts.[10] Moreover, this property could help the epoxidation of alkenes, because the easy dissociation of H_2 on the surface of gold can also favor the formation of peroxo species when oxygen is present. This peroxo moiety is very active in the epoxidation of propylene as in many other oxidation reactions.[1,26]

CONCLUSIONS

In summary, H_2 adsorption/dissociation was studied for bulk surfaces of gold and for nanoclusters from 14 to 29 gold atoms by DFT calculations. On bulk Au (111) and (100) surfaces no adsorption of molecular H_2 was observed. However, the results obtained for the nanoparticles predict a spontaneous dissociation of H_2 with stabilization energies of 30–40 kJ/mol. Different functionals were tried to model the chemisorption of molecular hydrogen on a Au_{29} cluster. Although the stabilization energies varied with the employed functional, all the results show the same mechanism of spontaneous dissociation of H_2.

It seems that several factors determine the ability of the particle to interact with hydrogen: low coordinated Au atoms, fluxionality, and ensemble effects. The flexibility of the structure, its adaptability towards the adsorbate plays a key role in the bonding and dissociation of H_2. And it appears that not only low coordinated Au atoms are needed because H_2 adsorption/dissociation is only seen when cooperation between several (4) active Au atoms is allowed.

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